Broadband Dielectric Study on Glass Transition of 1-Propanol-Water Mixtures

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Relaxation phenomena in various glass forming materials have been studied using dielectric, calorimetric, and other techniques. Dielectric measurements offer the advantage of obtaining precise data especially over a wide frequency range. A part of the glass forming materials indicates only one relaxation process observed in the high temperature range, and two relaxation processes observed in the low temperature range. The lower and higher frequency processes have been called the α- and β-processes, respectively. The β-process separates from the α-process at the crossover temperature, T_C. The β-process was observed for glass forming polymers, and supercooled state of simple liquids. However, the mechanism of the α-β separation for aqueous solutions has not been clarified yet.

We have carried out broadband dielectric measurements for aqueous solutions of polyalcohol, changing water content and molecular structure of the solute molecules systematically in 120 – 300 K, in order to clarify the mechanism of the α-β separation of the aqueous solutions. These water mixtures were ethyleneglycol-, glycerol-, and triethyleneglycol-water mixtures with various concentrations [1-4], and 65wt% ethyleneglycol oligomer (EGO)-water mixtures with various numbers of repeat units of EGO molecules [4,5]. For the alcohol- and smaller EGO-water mixtures, the solute molecules move cooperatively with water molecules in the whole temperature range measured, and this cooperative motion brings about the α-process, and the motion of the part of the water molecules leads to the β-process. In contrast, for the larger EGO-water mixtures, the solute molecule was too large to move cooperatively with the water molecules above T_C. However, the cooperative motion of part of the water molecules and solute molecules is possible below T_C. Then, this cooperative motion brings about the α-process, and the water molecules confined by the cooperative region contributing to the α-process brings about the β-process.

1-Propanol (PrOH) is one of the monohydric alcohols, and it can be easily supercooled. The PrOH shows three relaxation processes in low temperature range, and the molecular mechanism of these processes have been discussed. In this work, we performed broadband dielectric measurements for 1-propanol-water mixtures with various water contents, in order to clarify the molecular mechanism of the relaxation process related to the glass transition for monohydric alcohol-water mixtures.

Samples used in these experiments are 60-100 wt% PrOH-water mixtures. Complex permittivity of these mixtures was measured in the frequency range of 1 μHz and 30 GHz and in the temperature range of 78 K and 300 K. In order to cover the wide frequency range, we used five measuring systems. From 1 MHz to 30 GHz, Time Domain Reflectometry (TDR) method was employed. RF Impedance/Material analyzer (HP 4291A) was used between 1MHz and 1.8 GHz. LCR meter (HP 4284A) was used between 20 Hz and 1 MHz. From 2 mHz to 1 kHz and 1 μHz to 10 mHz, an AC phase Analysis (ACPA) and DC Transient Current (DCTC) method were employed, respectively.

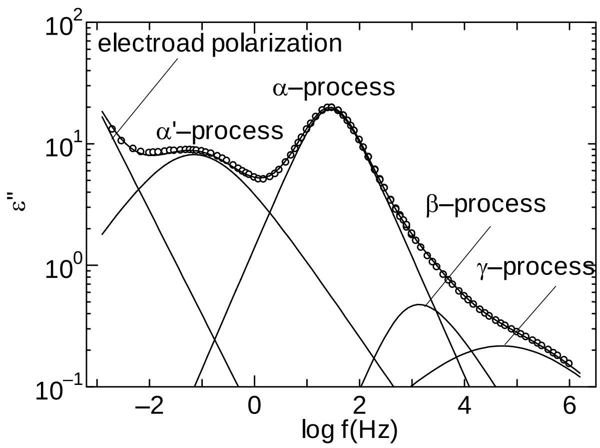

Figure 1. Frequency dependence of the dielectric loss for 80wt% 1-propanol-water mixture at 123 K.

Figure 1 shows plots of the frequency dependence of the dielectric loss for 80wt% PrOH-water mixture at 123 K, as example of the dielectric spectra below T_C. For the pure PrOH, Debye-type primary process and two small relaxation processes are observed in whole the temperature range measured. By adding water to PrOH, a KWW-type primary process and two small relaxation processes are observed at high temperature range, and another process is observed at lower frequency range than the primary loss peak at low temperature range, as shown in Fig. 1. We will discuss the molecular mechanism of the relaxation processes observed for the propanol-water mixtures from the water content dependence of the relaxation parameters.

References

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